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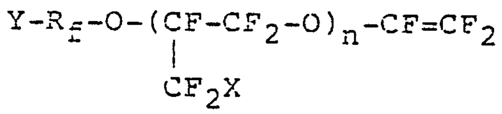
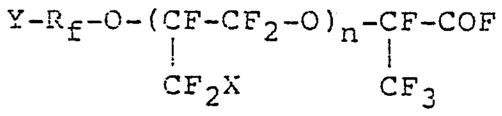
⑤④ Process for the preparation of fluoroalkyl perfluorovinyl ethers.

⑤⑦ The present invention relates to a process for the preparation of fluoroalkyl perfluorovinyl ethers of formula:



$$Y{-}R_f{-}O{-}(\underset{\displaystyle CF_2X}{CF}{-}CF_2{-}O)_n{-}CF{=}CF_2 \qquad (I)$$

wherein:
Y is Br or F;
X is F, Cl or Br or their mixtures when n is equal to or higher than 2;
n is comprised within the range of from 0 to 4;
R_f represents a perfluoroalkylene radical containing from 1 to 8 C atoms.
The process is characterized in that a fluoroalkoxy perfluoroacyl fluoride of formula:



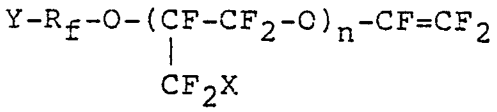
$$Y{-}R_f{-}O{-}(\underset{\displaystyle CF_2X}{CF}{-}CF_2{-}O)_n{-}\underset{\displaystyle CF_3}{CF}{-}COF \qquad (II)$$

is slowly heated with a salifying agent and a solvent, in the presence of catalytic amounts of N,N-

dimethylformamide, with an end temperature comprised within the range of from 60 to 150°C being reached.

PROCESS FOR THE PREPARATION OF FLUOROALKYL PERFLUOROVINYL ETHERS

The present invention relates to the preparation of fluoroalkyl perfluorovinyl ethers. More precisely, it relates to a process for the preparation of fluoroalkyl perfluorovinyl ethers having the formula:



$$Y-R_f-O-(\underset{CF_2X}{\underset{|}{CF}}-CF_2-O)_n-CF=CF_2 \qquad (I)$$

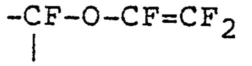
wherein:
Y is Br or F;
X is F, Cl or Br or their mixtures when $\underline{n}$ is equal to or higher than 2;
$\underline{n}$ is comprised within the range of from 0 to 4;
R_f represents a perfluoroalkylene radical containing from 1 to 8 C atoms.

The fluoroalkyl perfluorovinyl ethers are used as monomers for the copolymerization with fluorinated olefins, in particular tetrafluoroethylene, vinylidene fluoride and hexafluoropropene.

The introduction of the above said vinyl ethers in the so-obtained plastic polymers involves better properties of processability of the polymers, and a higher flexibility of the manufactured articles.

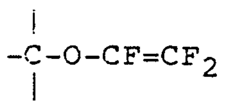
Furthermore when Y is Br, into the polymer a potentially reactive site is inserted, which can be used for additional reactions, which otherways would not be possible on perfluorinated materials. The obtained polymers can be used, e.g., in the chlorine-alkali cells as ion-exchange membranes.

The preparation is known of the fluoroalkyl perfluorovinyl ethers starting from the corresponding acyl fluorides,by decarboxylation of the acyl fluoride by heating up to 300°C in the presence of activators, such as ZnO and SiO_2, and possibly in the presence of salifying agents. But, such a synthesis route involves the formation of considerable amounts of secondary and tertiary isomers of the vinyl ether, as described in U.S. Pat. 3,896,179, i.e., compounds of type:



$$-\underset{|}{CF}-O-CF=CF_2$$

(secondary isomer)

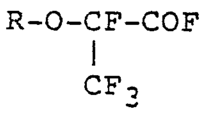


$$-\overset{|}{\underset{|}{C}}-O-CF=CF_2$$

(tertiary isomer)

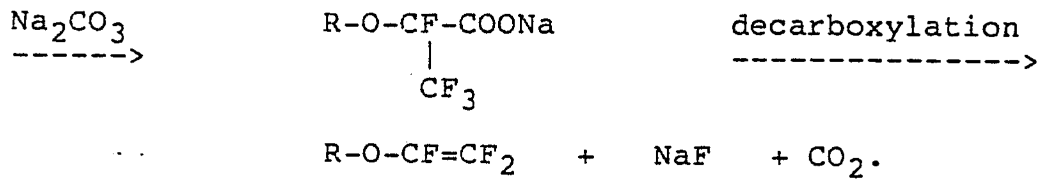
The presence of these isomers in the vinyl ether is highly undesirable, because they can act as chain-transfer agents in the subsequent copolymerizations, giving rise to copolymers with a too low molecular weight.

Also processes are known, which involve a salification of the acyl fluoride with salifying agents of the sodium carbonate type, in solvents of the glyme type, and a subsequent decarboxylation, e.g., at 100-150°C. These processes can be schematically shown as follows:



$$R-O-\underset{CF_3}{\underset{|}{CF}}-COF$$

wherein R is a fluoroalkyl radical



$$\xrightarrow{Na_2CO_3} R-O-\underset{CF_3}{\underset{|}{CF}}-COONa \xrightarrow{\text{decarboxylation}}$$

$$R-O-CF=CF_2 \quad + \quad NaF \quad + CO_2.$$

One of these processes is disclosed in U.S. Pat. 3,291,843.

When the vinyl ether is obtained by means of one of these processes, it can contain considerable amounts of hydrogenated byproduct, of the
$-CF_2-O-CFH-CF_3$
type.

The presence of hydrogenated products at a concentration higher than certain levels involves the presence of particularly reactive sites

$$\left(-\overset{|}{\underset{|}{C}}H \text{ bonds}\right),$$

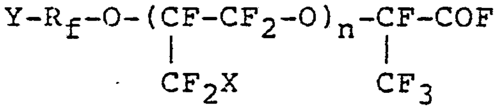
which are undesirable in the copolymerization process. It has been furthermore verified that copolymers obtained from vinyl ethers polluted by hydrogenated byproducts show insurmountable problems in the extrusion process, and lead to the obtention of manufactured articles having clearly unsatisfactory applicative properties.

A purpose of the present invention is to provide a process for the preparation of fluoroalkyl perfluorovinyl ethers of formula (I) by starting from the corresponding acyl fluorides, wherein the obtained product is free from secondary and tertiary isomers, and is substantially free from hydrogenated byproduct.

Another purpose is to provide a process which gives very high yields of fluoroalkyl perfluorovinyl ethers.

These, and still further purposes are achieved by the process of the present invention for the preparation of fluoroalkyl perfluorovinyl ethers of formula (I).

The process is characterized in that a fluoroalkoxy perfluoroacyl fluoride of formula:



$$Y-R_f-O-(\underset{\displaystyle CF_2X}{\underset{|}{CF}}-CF_2-O)_n-\underset{\displaystyle CF_3}{\underset{|}{CF}}-COF \qquad (II)$$

is slowly heated with a salifying agent and a solvent, in the presence of catalytic amounts of N,N-dimethylformamide, reaching an end temperature comprised within the range of from 60 to 150°C.

The Applicant has in fact found that by operating in the presence of catalytic amounts of N,N-dimethylformamide and slowly heating up to a temperature comprised within the range of from 60 to 150°C, the obtained product is free from secondary and tertiary isomers, and is substantially free from hydrogenated byproduct; and very high yields are furthermore obtained.

By the expression "substantially free" from hydrogenated byproduct, it is meant that such byproduct is present in a maximum amount not higher than 5% by weight in the reaction products. Often, it is present in an amount not higher than about 0.5% by weight.

The amount of N,N-dimethylformamide is generally comprised within the range of from 0.1 to 20% by weight relatively to the acyl fluoride (II) and preferably of from 0.5 to 5%.

The solvents are those used in the known art, in particular, those of the glyme type.

Also the salifying agents for the acyl fluoride (II) are those used in the known art, in particular the alkali-metal carbonates and alkali-earth metal carbonates are used.

The amount of salifying agent is not critical. It may range from the stoichiometric amount to an excess, e.g., of about 50%, relatively to the stoichiometric amount.

For the purpose of obtaining a vinyl ether endowed with a high purity level, it is necessary to thoroughly dry the solvent and the salifying agent.

Starting from an acyl fluoride (II) wherein the value of $\underline{n}$ is zero is preferred. Also starting from an acyl fluoride wherein the radical R_f contains from 2 to 3 C atoms is preferred.

The heating of the reaction mixture takes place slowly, until an end temperature comprised within the range of from 60 to 150°C, and preferably of from 110 to 140°C is reached. Usually, the heating of the reaction medium, to maintain it at the end temperature, is continued over a certain time, e.g. over from 2 to 8 hours. The duration of the slow heating step is, e.g., of from 1 to 6 hours.

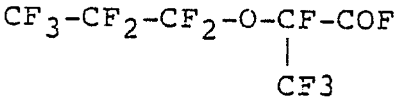
The following examples are supplied for the purpose of illustrating the invention without thereby limiting it.

Example 1

In the present example, to be compared to Example 2, N,N-dimethylformamide is not used.

To a 250-ml reactor equipped with stirrer, thermometer and distillation column with condenser, 50 ml of anhydrous diglyme and 50 g of anhydrous K_2CO_3 are charged.

At room temperature, 83 g (0.25 mol) of 2-perfluoropropoxy-perfluoropropionyl fluoride



$$CF_3-CF_2-CF_2-O-\underset{\displaystyle CF3}{\underset{|}{CF}}-COF$$

is slowly added, in such a way that the temperature of the reaction mixture doesn't exceed 30°C.

The reaction mass is then heated 1 hour at 35°C, then 1 hour at 45°C and 1 hour at 60°C; now, it is possible to start to draw the product refluxing through the distillation column.

For completing the reaction, the mixture is kept heated at 120°C for 6 hours.

Fifty-eight grams of a reaction product was obtained, which was identified by ^{1}H-N.M.R and ^{19}F-N.M.R. analyses, and mass-spectrophotometry.

80% of product is constituted by perfluoropropyl vinyl ether (46.4 g = 0.174 mol) and the residual 20% thereof is heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (C_3F_7-O-CFH-CF_3) (11.6 g). Reaction conversion = 100%, selectivity to and yield of perfluoropropyl vinyl ether = 69.7%.

During the reaction, small amounts of unidentified uncondensable products are formed.

Example 2

To a reaction equipment analogous to that as described in the preceding Example 1, 50 ml of anhydrous diglyme, 1 ml (0.994 g) of N,N-dimethylformamide and 50 g of anhydrous K_2CO_3 are charged.

At room temperature, 83 g (0.25 mol) of 2-perfluoropropoxy perfluoropropionyl fluoride is slowly added, in such a way that the temperature of the reaction mixture doesn't exceed 30°C.

The reaction mass is then heated 1 hour at 35°C, then 1 hour at 45°C and 1 hour at 60°C; now, it is possible to start to draw the product refluxing through the distillation column.

For completing the reaction, the mixture is kept heated at 120°C for 6 hours.

64.4 grams was obtained of a reaction mixture, which is constituted by:
64.07 g of perfluoropropyl vinyl ether;
0.32 g of heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether.

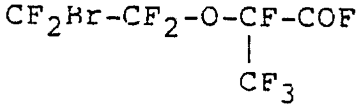
Conversion: 100%, selectivity to and yield of perfluoropropyl vinyl ester: 96%.

Example 3

In the present example, to be compared to Example 4, no N,N-dimethylformamide is used.

Five hundred ml of anhydrous diglyme and 400 g of anhydrous Na_2CO_3 are charged to a 2,000-ml four-neck flask equipped with stirrer, thermometer, dropping funnel and reflux condenser connected to a distillation Claisen apparatus.

860 g is added dropwise of acyl fluoride



$$CF_2Br-CF_2-O-\underset{\displaystyle CF_3}{\underset{|}{CF}}-COF$$

with the inner temperature being maintained at approximately 20°C. During the addition time, gas evolves. After dripping end, stirring is continued for 1 hour. The heating is then started, with the temperature being progressively increased up to 130°C: 1 hour at 80°C, 1 hour at 100°C, 1 hour at 120°C. The evolution of the gas starts again at 130°C. Now, it is possible to start to draw the product, which is collected inside a trap cooled at -78°C.

For completing the reaction, the reaction mixture is kept heated at 130°C for 3 hours.

The collected product is purified by fractional distillation. 400 grams is obtained of the fraction boiling at 56°-57°C, which contains 89.3% by weight of
$CF_2Br\text{-}CF_2\text{-}O\text{-}CF=CF_2$
and 10.7% by weight of
$CF_2Br\text{-}CF_2\text{-}O\text{-}CFH\text{-}CF_3$. .

The products were characterized by I.R. spectroscopy and ^{19}F-N.M.R. and ^{1}H-N.M.R.

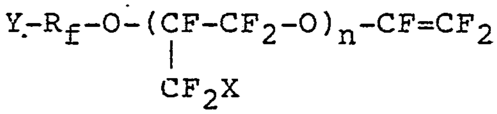
Example 4

The preparation is carried out according to the modalities of Example 3, by using 500 g of anhydrous Na_2CO_3, 600 ml of anhydrous diglyme, 1,000 g of the same acyl fluoride of Example 3, and 10 g of N,N-dimethylformamide. 650 g is obtained of a product, which is constituted by 96% by weight of
$CF_2Br\text{-}CF_2\text{-}O\text{-}CF=CF_2$
and 4% by weight of hydrogenated byproduct.

The products were characterized by I.R. spectroscopy and ^{19}F-N.M.R. and ^{1}H-N.M.R..

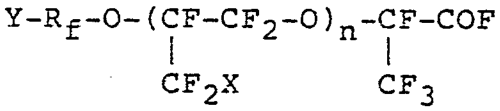
Claims

1. Process for the preparation of fluoroalkyl perfluorovinyl ethers of formula



$$Y\text{-}R_f\text{-}O\text{-}(\underset{\substack{|\\ CF_2X}}{CF}\text{-}CF_2\text{-}O)_n\text{-}CF=CF_2 \tag{I}$$

wherein:
Y is Br or F;
X is F, Cl or Br or their mixtures when n is equal to or higher than 2;
n is comprised within the range of from 0 to 4;
R_f represents a perfluoroalkylene radical containing from 1 to 8 C atoms;
characterized in that a fluoroalkoxy perfluoroacyl fluoride of formula:



$$Y\text{-}R_f\text{-}O\text{-}(\underset{\substack{|\\ CF_2X}}{CF}\text{-}CF_2\text{-}O)_n\text{-}\underset{\substack{|\\ CF_3}}{CF}\text{-}COF \tag{II}$$

is slowly heated with a salifying agent and a solvent, in the presence of catalytic amounts of N,N-dimethylformamide, with an end temperature comprised within the range of from 60 to 150°C being reached.

2. Process according to claim 1, characterized in that the amount of N,N-dimethylformamide is comprised within the range of from 0.1 to 20% by weight relative to the fluoralkoxy perfluoroacyl fluoride (II).

3. Process according to claim 2, characterized in that the amount of N,N-dimethylformamide is comprised within the range of from 0.5 to 5% by weight relative to the fluoroalkoxy perfluoroacyl fluoride (II).

4. Process according to one or more of the preceding claims characterized in that the solvent is selected from glymes.

5. Process according to one or more of the preceding claims, characterized in that the salifying agent is selected from carbonates of alkali metals or alkali-earth metals.

6. Process according to claim 5, characterized in that the salifying agent is an alkali-metal carbonate.

7. Process according to one or more of the preceding claims, characterized in that in the fluoroalkoxy perfluoroacyl fluoride (II), the value of n is zero.

8. Process according to one or more of the preceding claims, characterized in that in the fluoroalkoxy perfluoroacyl fluoride (II), the radical R_f contains from 2 to 3 C atoms.

9. Process according to one or more of the preceding claims, characterized in that an end temperature comprised within the range of from 110 to 140°C is reached.

10. Fluoroalkyl perfluorovinyl ethers of formula (I) obtainable by means of the process described in one or more of the preceding claims.